

SANS Study of Asphaltene Aggregation: Concentration and Solvent Quality Effects

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The structure of asphaltene solutions in toluene was studied by small-angle neutron scattering (SANS) as a function of temperature and concentration. Temperature alters solvent quality, flocculation being expected at low temperature. SANS measurements were carried out at four different temperatures (from 73 down to 8 °C) for solute (asphaltene) volume fractions Φ ranging from ≈ 0.3 to $\sim 10\%$. Asphaltenes were found to form nanometric aggregates, whose average masses (M_w) and radii of gyration (R_{GZ}) increased as temperature decreased. These parameters hardly varied with concentration in the dilute regime $\Phi \leq 3\text{--}4\%$, in which no evidence of dissociation was found. At higher Φ , apparent values of the same parameters (M_w and R_{GZ}) decreased as repulsive interactions or aggregate interpenetration reduced the normalized intensity, I/Φ , a phenomenon reminiscent of the semidilute regime of polymers and fractal aggregates. At the two lowest temperatures studied, 8 and 20 °C, a strong scattering at low q signaled flocculation, as some of the asphaltenes formed dense domains of micronic size. This phenomenon occurred throughout the studied concentration range and entailed some limited hysteresis for time scales of the order of a few hours.

Introduction

Asphaltenes,¹ defined as those compounds of petroleum that are insoluble in alkanes (such as *n*-pentane or *n*-heptane), are a mixture of polydisperse and chemically heterogeneous species. They comprise the heaviest, most polar, and richest in heteroatoms species of oil distillation residues. Their well-known tendency toward association or flocculation causes severe problems in oil production and in refinery processes and plays an important role in the rheology of heavy residues (asphalts) that are used as binders for road pavement materials.

A better understanding of asphaltene aggregation in natural or industrial oils and an improvement in the predictability of oil rheological properties are expected from a characterization of these macromolecular aggregates in their medium, using a simple physicochemical model with a few parameters. The experiments presented in this paper are a first step in that direction, as they demonstrate the applicability of macromolecular concepts such as solvent quality and overlap concentration to the description of asphaltene behavior in solution.

The quality of a solvent depends not only on its composition but also on the temperature (the effect of which is studied here) and the pressure. In oil production, the degradation in solvent quality is most often due to a pressure drop, while temperature and solvent composition vary to a lesser extent. A pressure decrease often induces an evolution similar to that encountered after a flocculant (such as *n*-pentane or *n*-heptane) is added or after the

mixture is cooled, with the appearance of large and dense asphaltene-rich domains causing reservoir and tube plugging.

Even in dilute solutions, asphaltenes form complex associations. At small-length scales (below about 100 Å), asphaltenes appear to dissociate into a few (2–6) smaller molecules if the concentration is very low (<0.5 wt %, typically, in aromatic solvents). Evidence for dissociation has been reported from surface tension,^{2–6} vapor pressure osmometry,^{7,6} or calorimetric⁸ measurements. It is not clear whether this association is micellar in nature.^{8,6} Because asphaltenes contain polynuclear aromatic parts, it has been suggested (but not firmly proved) that those sheets stack up like graphite layers (such planar elements forming the core of the “micelles”) surrounded by solvated (swollen) aliphatic/naphthenic tails.

Small-angle scattering measurements probe correlations between asphaltene-rich regions over distances ranging between a few and several thousand angstroms. Most of the measurements have concerned solutions with asphaltene concentrations of the order of 1%, below the concentration range ($\sim 5\%$ and above) where interactions

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between asphaltene-rich entities are expected to set in. The dilute solution approximation has often been employed to interpret the scattering spectra, with various and sometimes contradictory modeling schemes for representing these objects, including polydisperse dense flat objects,^{7,9,10} rods,¹¹ and spheres.^{12–14} Such ambiguities arise from attempts to fit the whole range of investigated wavevectors, q . Very often, the spectra exhibit a Guinier regime at low q , which allows a model-independent determination of certain averages of the radii and (if the scattering contrast is known) the molecular weights of asphaltene aggregates. Recently, a small-angle scattering study¹⁵ of asphaltenes in solvents of varying quality has shown that the molecular weight of the dilute aggregates varies approximately like the squared radius of gyration (see also ref 16). The solvent quality was controlled by varying the proportion of toluene (a solvent for asphaltenes) and heptane (a flocculant). The scattering results, combined with intrinsic viscosity measurements,¹⁵ point to a rather solvated and loose structure (fractal dimension ~ 2) for asphaltene aggregates. This work confirmed, in particular, the observations of ref 17, which combined light scattering, viscosimetry, and image analysis techniques (for the largest flocculated aggregates). The micelles, if different from the aggregates, could constitute their elementary units. Above a certain overlap concentration (of the order of a few percent), the aggregates interpenetrate, imparting high solution viscosities.¹⁵ In this regime, referred to as semidilute, small-angle scattering no longer probes the size and the molecular weight of individual aggregates but some correlation volume of concentration fluctuations. The scattering spectra still exhibit an apparent Guinier regime at low q in which “molecular weight” and “radius of gyration”, respectively, correspond to the mass and the size of a correlation domain of concentration fluctuations.^{18,15} Both parameters decrease as the concentration increases.¹⁸

The small-angle neutron scattering (SANS) measurements presented in this paper cover a large range of temperatures and asphaltene concentrations. The intensity of the neutron beam at Institut Laue-Langevin in Grenoble allowed us to carry out the measurements in the same experimental run, thus eliminating concerns for sample variability or aging. Because of the large scattering range of the small angle diffractometer D11 ($6 \times 10^{-3} \text{ \AA}^{-1} \leq q \leq 3 \times 10^{-1} \text{ \AA}^{-1}$, probing length scales 1/q from 5 to 1000 Å), structural evolution, as temperature and concentration varied, could be observed at length scales much larger than the individual aggregate size. Temperature varied from 73 °C, for which toluene is a good solvent, to 8 °C, when asphaltene flocculation sets in. Here, cooling had the same effect as adding a flocculant (e.g., *n*-pentane or *n*-heptane) to the solution. Concentration ranged from the very dilute regime ($\Phi \sim 0.3\%$), where dissociation effects may occur, to the concentrated regime

Table 1. Mass Concentration c and Temperature-Dependent Solute Volume Fraction Φ in the Nine Samples Studied by SANS

sample	c (%)	Φ (%)			
		$T = 8$ °C	$T = 20$ °C	$T = 40$ °C	$T = 73$ °C
1	13.15	10.69	10.61	10.44	10.17
2	9.80	7.91	7.85	7.72	7.513
3	6.56	5.26	5.21	5.13	4.99
4	4.20	3.35	3.32	3.27	3.17
5	2.95	2.35	2.33	2.29	2.22
6	1.81	1.44	1.42	1.40	1.36
7	1.08	0.852	0.844	0.830	0.806
8	0.538	0.426	0.422	0.415	0.403
9	0.387	0.306	0.304	0.298	0.290

($\Phi \sim 10\%$), where interactions between aggregates should exert a strong influence on the structure.

Thus, these experiments provide insight into the concentration dependence of asphaltenes in solution and, in particular, allow us to delineate the extent of the dilute concentration regime (in which aggregates appear to behave as stable independent entities). Then, they shed some light on the phenomenon of asphaltene flocculation, as the colloidal structure changes over different length scales in response to cooling.

The outline of the paper is as follows. After the materials utilized and the necessary elements of the SANS technique (such as the evaluation of the scattering contrast) are presented, we display the qualitative features of the measured scattering spectra. These spectra all exhibit a Guinier plateau, to which a strong low- q upturn is superimposed at the lowest temperatures because of the presence of a flocculating, asphaltene-rich phase. From the Guinier regime, we extract the apparent aggregate molecular weights and radii of gyration, which are presented and discussed as a function of temperature and concentration. Then, the large-scale features (corresponding to the low- q region of the spectra) that appear at low temperatures are analyzed and interpreted in terms of phase separation.

Materials and Methods

Sample Preparation and Characterization. Asphaltenes were extracted from a heavy Arabian vacuum residue (Safaniya) by precipitation with *n*-heptane (according to the standard NF T60-115 method). The asphaltene amount is 15 wt % of the residue. The elemental analysis of the asphaltenes yields the following (molar) composition in atomic constituents: carbon, 46.5%; hydrogen, 50.8%; sulfur, 1.6%; nitrogen, 0.5%; and oxygen, 0.6%.

We used perdeuterated toluene as a solvent to have a sufficient coherent neutron scattering length difference between the solute and the solvent. Asphaltene solutions were prepared by dispersing the appropriate amount of asphaltenes in the solvent and then allowing them to rest overnight. The solutions were loaded into quartz cells of 1 or 2 mm path length, which were then flame-sealed. Table 1 gives the mass concentration and the asphaltene volume fraction of the samples that were studied by SANS together with the temperature of the measurements. The volume fraction depends somewhat on temperature because the ratio of asphaltene to toluene mass densities changes with the temperature. Asphaltene mass densities were extrapolated from the linear variation of the densities of the solutions with the asphaltene weight fraction and found to be a very slowly decreasing function of temperature, from $\rho_m^A = 1.210 \text{ g/cm}^3$ at 8 °C to $\rho_m^A = 1.189 \text{ g/cm}^3$ at 73 °C.

SANS. SANS experiments were performed at Institut Laue-Langevin in Grenoble, France, using the D11 diffractometer. Sample-to-detector distances of 2.5, 13, and 35.7 m and neutron wavelengths of, respectively, $\lambda = 6, 6,$ and 8 \AA resulted in an experimental q range of $1.2 \times 10^{-3} - 0.15 \text{ \AA}^{-1}$. All data were converted to an absolute scale with reference to a water standard,

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following the same procedure as in ref 19, where measurements on the same apparatus are reported. The data have been corrected for detector dead time effects, and contributions due to solvent incoherent scattering have been subtracted out, while the incoherent signal of the solute has been neglected.

The interpretation of the scattering data relies on the classical assumption that the scattering length density is constant within both phases, the solvent, and the asphaltene particles (or the aggregates), regarded as continuous media on the scale of the scattering wavelength. The measured scattering cross-section $I(q)$ is then proportional to the static structure factor of the asphaltenes (equal to the Fourier transform of the autocorrelation function of the asphaltene phase). The proportionality factor or the scattering contrast term K is the squared scattering length density excess of solute (asphaltene) with respect to solvent:

$$K = (\rho_A - \rho_S)^2$$

The (coherent) scattering length densities are calculated as follows:

$$\rho = \rho_m \sum_i \frac{x_i}{m_i}$$

where x_i , m_i , and b_i are, respectively, the mass fraction, mass, and scattering length of atoms of species i , while ρ_m denotes the mass density of the medium.

Using the measured elemental composition and the mass densities for our asphaltenes, we obtain values for the contrast term varying from $K = 1.88 \times 10^{21} \text{ cm}^{-4}$ at 8 °C to $K = 1.56 \times 10^{21} \text{ cm}^{-4}$ at 73 °C.

$I(q)$ provides information on the structure of the solutions on the scale $1/q$. Dilute solutions in which correlations between different particles can be ignored yield a signal proportional to the solute volume fraction Φ . Specifically, one has

$$\frac{I(q)}{K\Phi} = \frac{M_w}{\rho_m^A} \langle F(q) \rangle_Z \quad (1)$$

In eq 1, M_w is the weight average of the mass of solute particles; $F(q)$ is the form factor or the scattering function of one particle, which is characteristic of its shape and internal structure; and $\langle \dots \rangle_Z$ is a notation for the "Z-average" that is defined, for any quantity a , as

$$\langle a \rangle_Z = \frac{\langle M^2 a \rangle}{\langle M^2 \rangle}$$

While M_w is an average of the mass of asphaltene material contained in one particle, an indication of the overall size of the volume occupied in the solution is given by its radius of gyration, R_G . R_G appears in the small q ($qR_G \ll 1$), or Guinier regime, behavior of $F(q)$:

$$F(q) = 1 - \frac{q^2 R_G^2}{3} + O(q^4)$$

A scattering signal approaching a constant a at low q as

$$\frac{I(q)}{K\Phi} \approx a - bq^2 \quad (2)$$

might thus be interpreted, in a dilute solution, as the Guinier regime of a collection of uncorrelated particles for which the weight-averaged mass is given by

$$M_w = \rho_m^A a \quad (3)$$

while the Z-average of the squared radius of gyration is identified as

$$R_{GZ}^2 = 3b/a \quad (4)$$

Alternatively, one may resort to the Zimm formula:

$$\frac{K\Phi}{I(q)} \approx \frac{\rho_m^A}{M_w} \left(1 + \frac{q^2 R_{GZ}^2}{3} \right) \quad (5)$$

Although it is of course equivalent, in principle, to eqs 2–4, we found that Zimm's form (eq 5) eased the identification of parameters M_w and R_{GZ} , since it fits the spectra on a wider q interval. This is further discussed in the section on the Quantitative Analysis of the Guinier Regime.

In the present study, we systematically resort to the Zimm formula to fit all asphaltene spectra in the plateau region. The parameters M_w and R_{GZ} that are obtained outside the dilute concentration range, when $I(q)$ is not proportional to Φ , are referred to as apparent masses and radii of gyration.

Results and Discussion

The measured SANS spectra of the asphaltene solutions investigated all displayed the same general qualitative temperature and wavevector dependences. For instance, the scattering spectra obtained at all four temperatures for a rather low ($c = 1.81 \text{ wt } \%$) and a moderate ($c = 6.56 \text{ wt } \%$) concentration (see Table 1) are shown in Figure 1. Over the whole range of wavevectors q , three regions can be distinguished.

(i) For $q \geq 3 \times 10^{-2} \text{ \AA}^{-1}$, the scattered intensity is a fastly decreasing function of q , the slope of the spectrum on a double logarithmic plot varying typically between 2 and 2.5. The shape of such $I(q)$ vs q plots, if solute particles (or aggregates) behave as independent objects, is characteristic of the shape, the internal structure, and the polydispersity of those particles.

(ii) In the intermediate or Guinier region, $10^{-2} \text{ \AA}^{-1} \leq q \leq 3 \times 10^{-2} \text{ \AA}^{-1}$, the intensity levels off to a plateau value, from which the average masses (M_w) and the radii of gyration (R_{GZ}) of the aggregates are extracted.

(iii) For $q \leq 10^{-2} \text{ \AA}^{-1}$, at the two lowest temperatures, 8 and 20 °C, the intensity $I(q)$ strongly increases with the length scale q^{-1} , an evidence for the appearance of large-scale ($\geq 100 \text{ \AA}$), asphaltene-rich heterogeneities.

As intensities on Figure 1 are normalized by the contrast term and asphaltene volume fraction Φ , the observed temperature dependence of the spectra is related to structural evolution. While the most important temperature effect occurs at large scale ($q \leq 10^{-2} \text{ \AA}^{-1}$) for $T \leq 20 \text{ °C}$, some effect is apparent in the intermediate regime, where the plateau intensity, equal to the apparent aggregate volume $V_w = M_w/\rho_m^A$, is a decreasing function of temperature. At higher q values, though, our measurements show no appreciable temperature influence, indicating that the internal, small-scale structure of asphaltene aggregates is unaltered.

Some of the concentration effects are illustrated by Figure 2, which displays the scattering spectra of all solutions at $T = 73 \text{ °C}$. The strong low- q scattering is absent at this temperature (see Figure 1), and the corresponding part of the spectra is therefore not shown. Again, small-scale features $q \geq 3 \times 10^{-2} \text{ \AA}^{-1}$ of asphaltene aggregates are not sensitive to concentration. In the intermediate (Guinier) region, the normalized intensities $I(q)/K\Phi$ superimpose for low-volume fractions (Φ below 3–4%), meaning that aggregates scatter independently (dilute concentration regime), while $I(q)/K\Phi$ is reduced by interactions for Φ above 3–4% (semidilute regime). In the following, we present and discuss the results in a more quantitative fashion, focusing first on the small- and intermediate-length scales ($q^{-1} \leq 100 \text{ \AA}$, Guinier regime)

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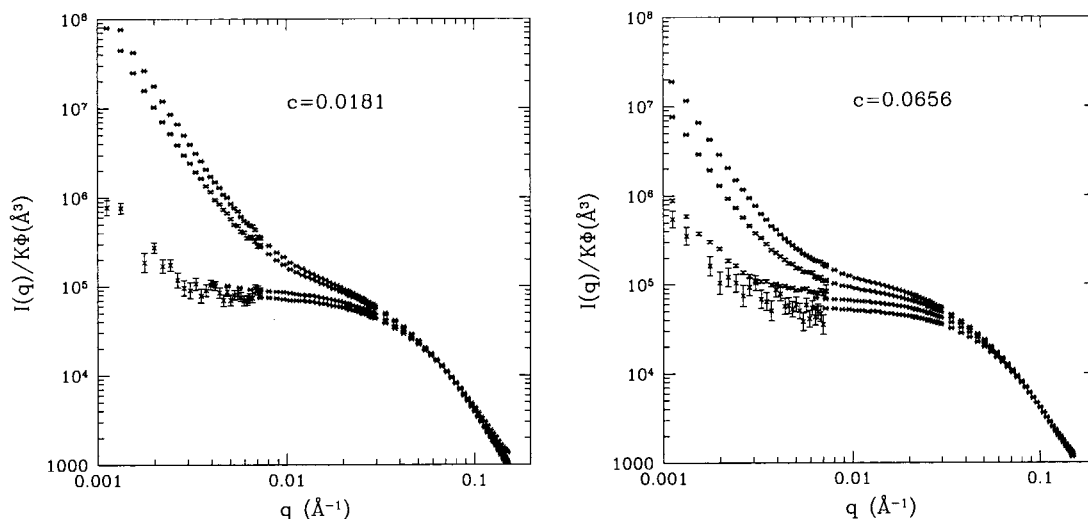


Figure 1. Normalized scattering spectra for two different (mass) concentrations c for the four temperatures (from bottom to top) 73, 40, 20, and 8 °C. The left plot corresponds to sample 6, and the right one corresponds to sample 3. Note that error bars are smaller than symbols, except for the low- q spectra at the highest temperature for which a limited beam time was spent.

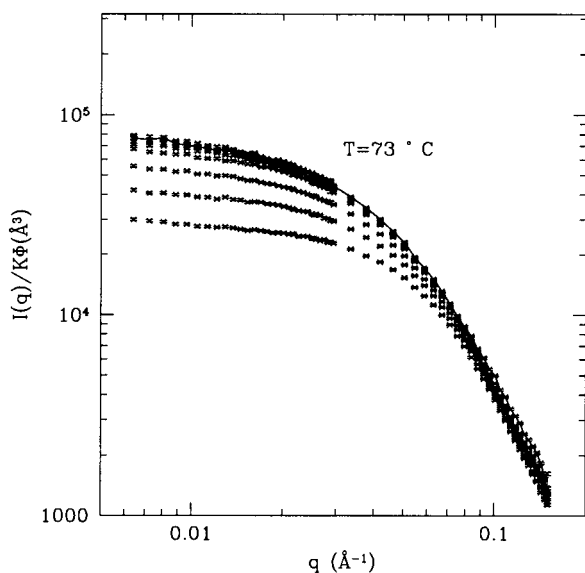


Figure 2. Normalized scattering spectra at 73 °C for all 9 solutions. In the $q \sim 10^{-2} \text{ \AA}^{-1}$ range, the normalized intensity is a decreasing function of concentration: the lowest data points thus correspond to sample 1. The data points joined by a continuous line are those of the most dilute sample ($c = 0.387\%$, $\phi = 2.896 \cdot 10^{-3}$).

structure of asphaltene aggregates and then on the large-scale ($\geq 100 \text{ \AA}$) features that accompany flocculation.

Quantitative Analysis of the Guinier Regime. As mentioned above, the intermediate (Guinier) region of the scattering spectra has been treated using Zimm's (eq 5) functional form. This enables the evaluation of M_w and R_{GZ} , even at the lowest temperatures when the Guinier plateau is partly hidden by the signal due to large-scale inhomogeneities. This point is further discussed in the following paragraph. The temperature and concentration dependences of both parameters that are presented in Figures 4 and 5 are then analyzed and discussed.

Use of the Zimm Formula. Extracting average molecular masses and radii of gyration of asphaltene particles at 8 and 20 °C is rendered difficult, as the plateau corresponding to the Guinier regime overlaps with the low- q upturn of the scattered signal. However, this problem is apparently less acute at 40 and 73 °C. At those latter

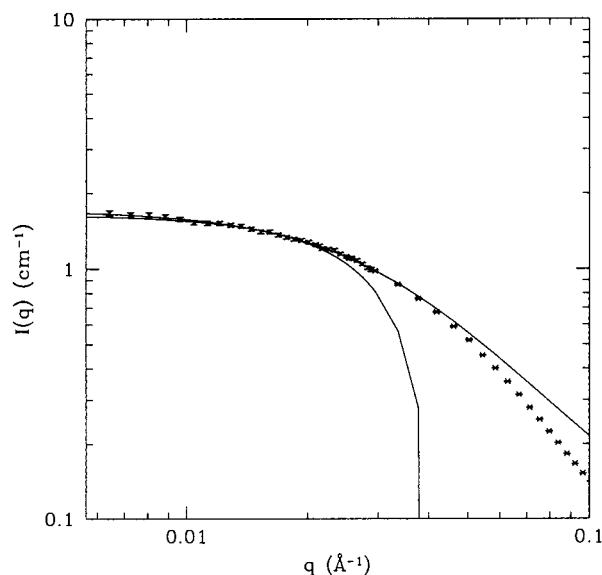


Figure 3. Comparison of eqs 2 and 5 in the Guinier regime (sample 6 at 73 °C). A fit to eq 5 (upper curve) has a wider range of validity.

temperatures, one can successfully, within a restricted q interval (say $0.01 \text{ \AA}^{-1} \leq q \leq 0.02 \text{ \AA}^{-1}$) directly fit the spectra to the Guinier form, as in eq 2. However, the Zimm formula, eq 5, which was already used in ref 15 for asphaltene solutions, fits the data on a larger interval, as shown in Figure 3. This advantage has been exploited in the present study: the influence of the intensity increase at low q (due to phase coexistence) for the lower temperatures is much smaller at higher wavenumbers. When eq 2 fails, for lack of a sufficiently well-defined plateau in the range $0.01 \text{ \AA}^{-1} \leq q \leq 0.02 \text{ \AA}^{-1}$, eq 5 (the Zimm form) still provides a satisfactory fit in the interval $0.02 \text{ \AA}^{-1} \leq q \leq 0.04 \text{ \AA}^{-1}$. Therefore, all quoted values of M_w and R_{GZ} in the present paper were obtained with eq 5.

One must be aware that the Zimm formula (eq 5) involves some amount of data modeling, if it is used outside the $q \ll 1/R_G$ range. It happens to correctly describe the scattering spectra of the asphaltene solutions that are studied here because of the specific shape (and, possibly, polydispersity) of the solute particles. It was first introduced for polymer coils²⁵ and later proposed for fractal

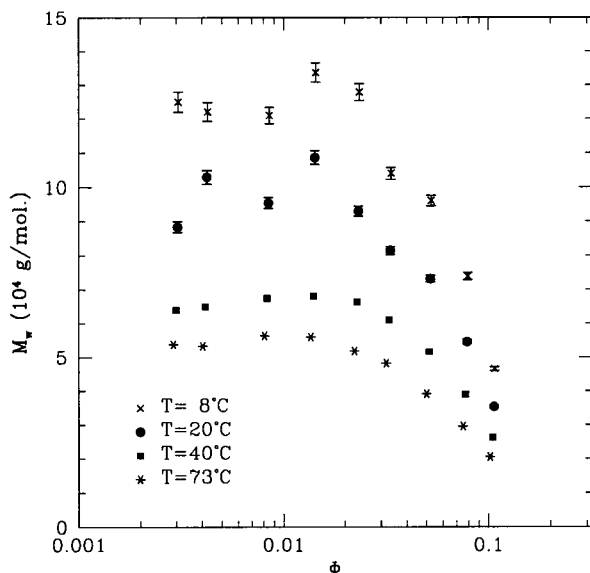


Figure 4. Apparent weight-averaged molar mass M_w , as obtained with the Zimm formula, as a function of solute volume fraction Φ for all four temperatures. Larger values recorded for samples 6 and 8 at the lower temperatures are probably due to contamination of the Guinier regime signal by the low- q feature, which is especially strong in those two cases. (Error bars are not shown when they are smaller than the symbols).

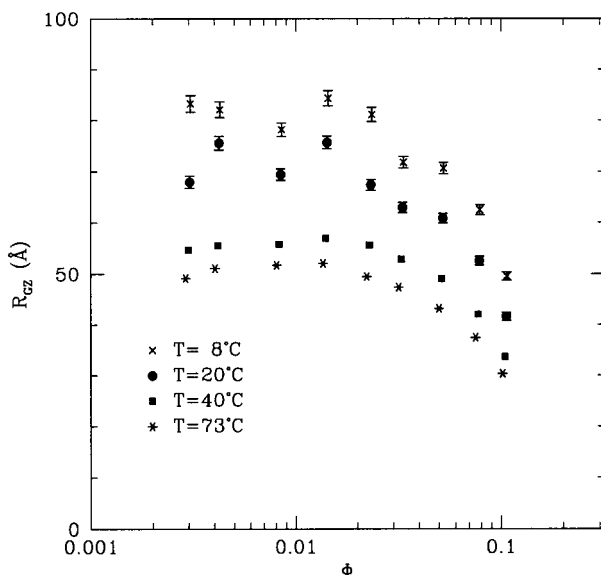


Figure 5. Apparent radius of gyration R_{GZ} , as obtained with the Zimm formula, as a function of solute volume fraction Φ .

objects of dimension two.²⁶ Such uses of eq 5 are consistent with the interpretation of the measurements we put forth here, regarding asphaltene aggregates as tenuous, fractal structures with dimension ≈ 2 .

As Table 2 shows, both procedures, when applicable (i.e., at high temperature), yield similar trends for M_w

Table 2. Apparent Masses and Radii of Gyration^a

sample	$T = 73^\circ\text{C}$ Φ (%)	Guinier (eq 2)		Zimm (eq 5)	
		M_w (g/mol)	R_{GZ} (Å)	M_w (g/mol)	R_{GZ} (Å)
1	10.17	20 500	29.2	20 600	30.4
2	7.41	28 900	31.7	29 600	37.5
3	4.99	38 300	37.5	39 100	43.2
4	3.17	46 300	38.3	48 200	47.3
5	2.22	50 100	41.1	51 800	49.4
6	1.36	53 800	42.5	56 000	52.0
7	0.806	54 600	43.6	56 300	51.7
8	0.403	51 800	43.1	53 300	51.1
9	0.297	52 700	43.1	53 800	49.1

^a Apparent parameters M_w and R_{GZ} as obtained from fits to the scattering spectra at 73°C using eq 2 in the interval $0.01 \text{ \AA}^{-1} \leq q \leq 0.02 \text{ \AA}^{-1}$ and eq 5 in the interval $0.009 \text{ \AA}^{-1} \leq q \leq 0.04 \text{ \AA}^{-1}$. Both procedures yield good "quality of fitting" likelihood parameters and uncertainties less than 500 g/mol for M_w and smaller than 2 Å for R_{GZ} .

and R_{GZ} as a function of concentration, even though values obtained using Zimm's formula (eq 5) are consistently above those inferred using eq 2. It should be noted that, on resorting to the Zimm form for the scattering signal of what is assumed to be a polydisperse collection of fractal aggregates of dimension two, we identify some effective radius of gyration R_{GZ}^{Zimm} that, due to the convexity of the function $\xi \rightarrow 1/(1 + \xi^2 q^2)$, underestimates the true R_{GZ} . That R_{GZ}^{Zimm} is larger than the value of R_{GZ} obtained with eq 2 might thus be attributed to a remaining influence of the small low- q upturn of the signal, which tends to decrease the downward curvature of $I(q)$ in the Guinier range.

Temperature Effects. Temperature reduces the degree of aggregation of asphaltenes. This trend is obvious from Figure 1, as the normalized scattering intensity $I(q)/K$ is a decreasing function of temperature. Molecular weights, as measured in dilute solutions (Figure 4), decrease from 130 000 at 8°C to 50 000 at 73°C , while the corresponding radii of gyration (Figure 5) decrease from 80 to 50 Å.

These results are consistent with those of previous temperature-dependent SANS studies. Overfield and co-workers²⁰ observed a similar decrease in aggregate size and molecular weight after dilute ($c = 1 \text{ wt } \%$) asphaltenes in toluene were heated from 25 to 100°C . In a more extensive study on dilute asphaltenes ($c = 5 \text{ wt } \%$) in methylnaphthalene, Thiyagarajan et al. monitored the scattering intensity decrease as the temperature was raised from 20 to 400°C . They noticed substantial drops in radii of gyration and molecular weights (or forward scattering $I(q \rightarrow 0)$) between 20 and 50°C and then a more progressive decrease at higher temperatures. In view of those scattering data, it is likely that 20°C was close to the flocculation threshold for the asphaltene-solvent system investigated.

As a rule, the influence of temperature on aggregate size and weight is somewhat weaker than that of solvent composition. While the molecular weights vary by a factor of 2.5 in the present study, a 10-fold increase of aggregate weight was observed for similar asphaltenes as the heptane content of the solvent mixture approached the flocculation threshold.¹⁵

Concentration Effects. At all four temperatures, the evolution of the apparent parameters M_w and R_{GZ} with volume fraction Φ , as displayed in Figures 4 and 5, is approximately the same: consistent with the normalized spectra shown in Figure 2, their values are nearly constant below $\Phi = 3\text{--}4\%$ and steadily decrease above $3\text{--}4\%$. No evidence of asphaltene dissociation after dilution is found here: asphaltene particles behave as stable entities, keeping the same structure down to $\Phi \approx 0.3\%$.

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Again, the results agree with those from previous concentration-dependent SANS studies. Ravey et al.⁹ measured the SANS spectra for several solutions of Safaniya asphaltenes in tetrahydrofuran. After taking the data of their Figure 5 and dividing $I(q)$ by concentration c , we found that the normalized forward scattering intensity $I(q \rightarrow 0)/c$ stayed roughly constant from $c = 0.2$ to 2.3 wt %. It should be recalled that cmc values, as obtained by tensiometry^{2,7} or calorimetry,⁸ are below $c = 0.35$ wt %, which is outside the range investigated here.

In the semidilute regime, for $\Phi \geq 3\text{--}4\%$, both parameters M_w and R_{GZ} decrease (Figures 4 and 5). Because we regard asphaltene particles as swollen, tenuous aggregates characterized by a fractal dimension D around 2,^{15,18} the general scaling laws pertaining to semidilute solutions of such soft fractal objects should apply.

Such scaling laws can be heuristically inferred within the "blob" picture:²¹ when Φ is large enough for aggregates to overlap, the solution can be regarded as an assembly of blobs, or correlation domains, of size $\xi \propto R_G$. Over length scales larger than ξ , it appears to be homogeneous, i.e., density fluctuations are not correlated. As blobs are representative volumes for the evaluation of the average concentration, one should have

$$\Phi \propto \xi^{D-3} \text{ or } \xi \propto \Phi^{-1/(3-D)}$$

Below the blob scale, concentration correlations are those of a fractal object of dimension D ; therefore, the apparent mass, or $I(q \rightarrow 0)/\Phi$, satisfies

$$M_w \propto R_{GZ}^D \quad (6)$$

Consequently, it relates to Φ as

$$M_w \propto \Phi^{-D/(3-D)} \quad (7)$$

The Zimm formula, eq 5, corresponds to an exponentially decreasing concentration correlation function of the Ornstein–Zernike form²² $\exp(-r/\xi)/r$, with $\xi^2 = R_G^2/3$.

The scaling laws (such as eqs 6 and 7) are quite insensitive to the precise nature of the interpenetrating fractal objects (e.g., independent or cross-linked polymers or various types of clusters resulting from a kinetic aggregation process). This universality is especially valuable with asphaltene solutions because it enables us to ignore the tremendous complexity of asphaltene chemistry. We therefore attempted a direct test of eqs 6 and 7, despite the relatively small degree of aggregation of asphaltene particles.

Measured values of M_w are represented as a function of R_{GZ} in Figure 6, showing that eq 6 is roughly satisfied with $D \approx 2$ at each temperature. The same scaling behavior was observed¹⁵ when the variation in aggregate mass and size is caused by the addition of a flocculant (e.g., *n*-heptane) to the solution. As for eq 7, we note that its range of validity is necessarily quite restricted. On one hand, it cannot of course be satisfied in the dilute regime (in which $M_w = M_w^{\text{dilute}}$ does not depend on Φ): this requires M_w to be small enough as compared to the aggregate mass M_w^{dilute} ; on the other hand, the correlation length, or R_G , has to be significantly larger than the size of the elementary unit for a scaling law to make sense. As the molar mass of some individual aggregating units could already be of order 10^4 , the scaling regime cannot be developed on a wide range. However, Figure 7 shows that eq 7 gives the correct trend in the semidilute regime at the two lowest temperatures for the higher concentrations.

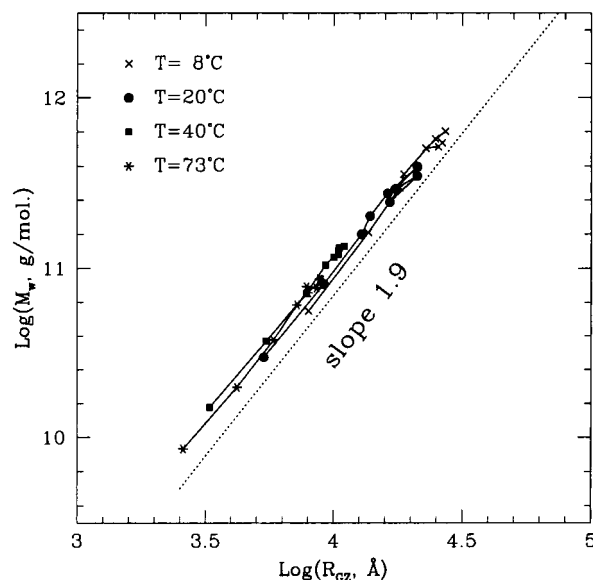


Figure 6. $\ln(M_w)$ versus $\ln(R_{GZ})$ (natural logarithms) for all solutions at all four temperatures. Data corresponding to the same temperature are joined by continuous lines. Results are compatible with eq 6.

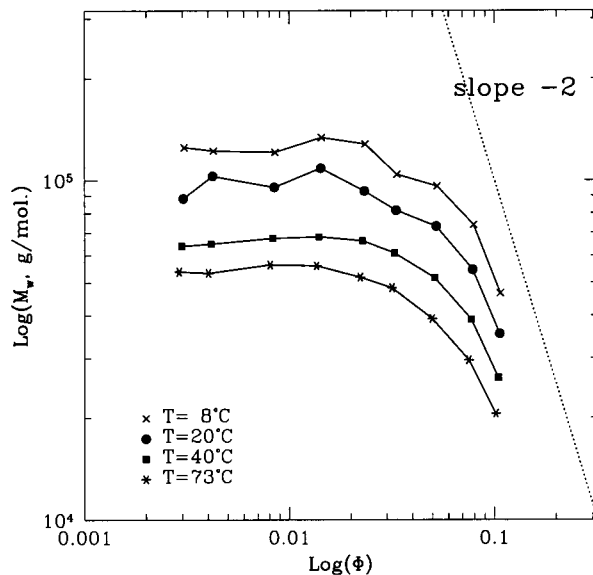


Figure 7. Same data as Figure 4, on a doubly logarithmic plot. The straight line corresponds to eq 7 with $D = 2$.

Large-Scale Heterogeneities. We have observed that the low- q part of the spectra measured at 8 °C, if measured several hours after the temperature quench, is a slowly decreasing function of time. Necessarily, an increase occurred at earlier times, but this stage of the evolution has not been recorded.

Figure 8 displays the normalized scattering intensity of samples 1, 3, 5, 6, and 8 at 8 °C. The low- q part of these spectra was recorded 7 h after the temperature change. Within this set of data, $I(q)/\Phi$ at low q is a decreasing function of concentration. This apparent concentration dependence might be due to a kinetic effect: the intensity could decrease faster in time in more concentrated solutions. The low- q upturn at 8 °C was fit to a power law, the parameters of which are given in Table 3:

$$\frac{I(q)}{K\Phi} = Aq^{-\alpha} \quad (8)$$

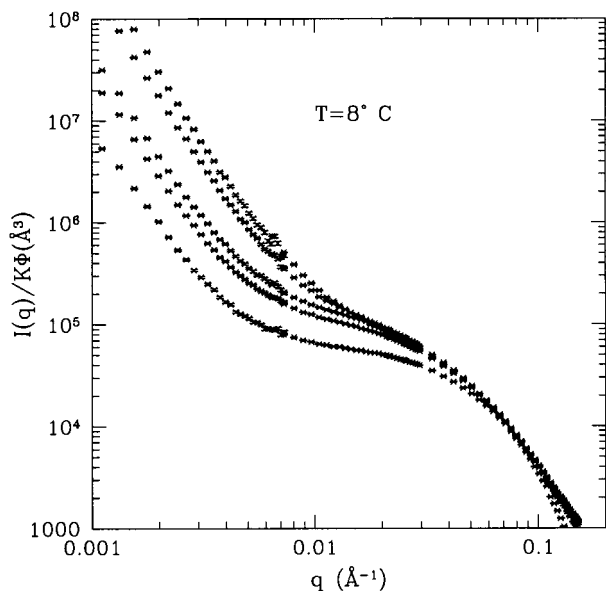


Figure 8. Normalized scattering spectra at 8 °C for samples 1, 3, 5, 6, and 8 (see Table 3). The intensity at small q is a decreasing function of concentration.

Table 3. Small q Signal at 8 °C^a

sample	$I(q_1)/\Phi$ (cm ⁻¹)	α
1	6.36×10^3	3.11
3	2.18×10^4	3.39
5	3.53×10^4	3.48
6	1.44×10^5	3.61
8	2.86×10^5	3.90

^a Characteristics of the low- q spectra at $T = 8$ °C, shown in Figure 8. α is the exponent in eq 8, fit to the data points between $1.2 \times$ and $2.4 \times 10^{-3} \text{ \AA}^{-1}$. $q_1 = 1.33 \times 10^{-3} \text{ \AA}^{-1}$ is the scattering wavenumber corresponding to the second data point on the spectra for the chosen device configuration. See Table 1 for sample concentrations.

From Table 3, it appears that the stronger the low- q intensity, the closer to 4 is the fitting exponent α of eq 8.

We interpret this low- q signal to the formation of asphaltene-rich domains: a phase separation phenomenon occurs at low temperature, whatever the concentration in the investigated range. As dense domains form, the characteristic signal of the interface appears in the spectrum. Departures from the Porod law ($\alpha = 4$) might be attributed to lack of sharpness or curvature of this surface as aggregation of dense domains proceeds. Because there is no evidence of bending toward a Guinier plateau at the lowest accessible q (10^{-3} \AA^{-1}), these domains are larger than 0.1 \mu m .

This phase separation process can explain the time dependence of our measurements. Phase separation is bound to be influenced by kinetics, and pure equilibrium thermodynamics is of limited relevance for the prediction of such slow, large-scale phenomena as the spatial organization of two-phase textures. The decrease in time of the signal might be due to the gathering of small dense domains to form larger regions, thus reducing the specific surface area of the interface. (In the later stages of phase separation, some sedimentation of the denser phase may also occur and could contribute to the lowering of the small wavevector signal. However, as the intensity at large q does not decrease, this phenomenon should only involve a negligible amount of solute). Moreover, time evolutions are understandably faster in more concentrated solutions in which diffusion-limited processes are more efficient.

As the large-scale structure of the flocculating asphaltene solutions depends on time, it should also be affected

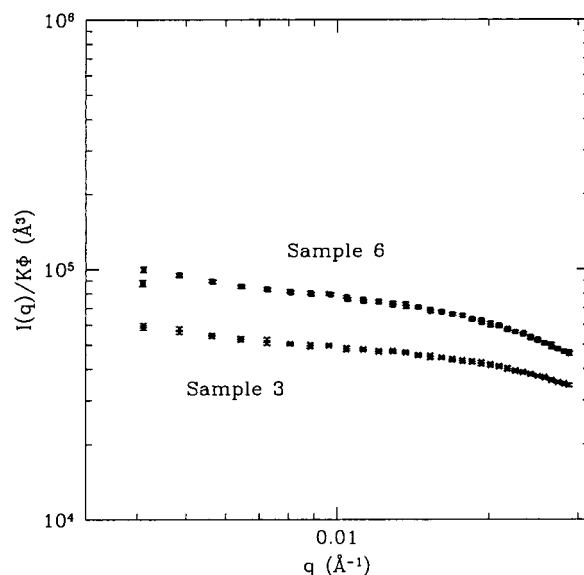


Figure 9. Normalized spectra, in the intermediate q range, of sample 3 at 73 °C and sample 6 at 40 °C, before and after being cooled to 8 °C. In both cases, data almost perfectly superimpose, and scattering signals are insensitive to temperature history.

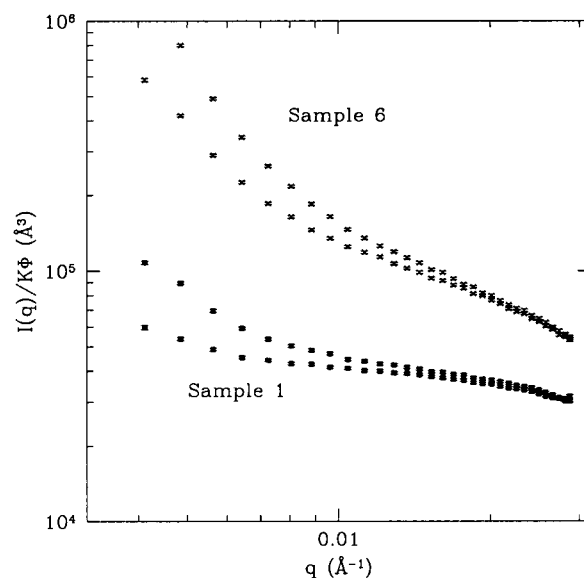


Figure 10. Normalized scattering spectra, in the intermediate q range, at 20 °C for two samples before and after being cooled to 8 °C for about 12 h. The latter signal is stronger for $q \leq 2 \times 10^{-2} \text{ \AA}^{-1}$, indicating a persistence of the large-scale heterogeneities that appeared at the lowest temperature.

by the cooling history. As shown in Figure 9, the spectra exhibit no significant history dependence at $T = 73$ and 40 °C: intermediate q spectra for samples 3 and 6 are indistinguishable before and after cooling at 8 °C for 12 h (Figure 9). As for the low- q signal at the highest temperatures, we found it to be very weak anyway (see Figure 1). Intensities at 20 °C, on the other hand, differ before and after cooling to 8 °C for wavenumbers smaller than about $2 \times 10^{-2} \text{ \AA}^{-1}$. This is apparent in Figure 10, which also shows, however, that the hysteresis does not extend to larger wavenumbers.

Summary and Conclusion

The following picture of asphaltene structural evolution with concentration and solvent quality emerges from the

SANS experiments reported and discussed in this paper. In the dilute concentration regime, which, for the asphaltene investigated, covers a range of volume fractions from 0.3 to 3–4%, asphaltene aggregates appear as stable solvated entities with molecular weights of the order of 10^5 g/mol and radii of gyration of a few nanometers. In the semidilute concentration regime (corresponding to volume fractions >3 –4% for the asphaltene investigated in this study), those aggregates interpenetrate, the measured molecular weights and radii of gyration are those of a correlation volume of concentration fluctuations (blob), and they decrease with increasing concentration. We expect that asphaltene in crude oils or in the various industrially processed petroleum fractions also exhibit an overlap concentration above which the viscosity should increase very rapidly with asphaltene concentration.

With decreasing solvent quality, the aggregates (or the blobs in the semidilute regime) grow, but their small-scale internal structure is unchanged. Flocculation is characterized by the appearance of a phase consisting of dense (i.e., asphaltene-rich) and large (>0.1 μm) domains, accompanied by kinetic effects on the hour scale, that we attribute to texture coarsening and rearrangements.

Instead of varying the temperature, as we did in the present study, one more often, in practice, uses the flocculant content of the solution as the control parameter for solvent quality.^{17,15} Typically, a varying amount of, for example, a low molecular weight alkane such as *n*-heptane

or *n*-pentane, is added to the mixture until asphaltene flocculation occurs. In previous SANS experiments, we attempted to follow asphaltene aggregation triggered by the addition of heptane^{23,24} but were unable to obtain reproducible and stable results for the spectra. In fact, solutions were either stable (at low enough heptane content in the solvent) or unstable (at higher heptane content) with, in the latter case, a rapid evolution similar to that observed here at 8 °C: the low- q intensity first fastly grows in time (within 1 h) and then decreases. Very likely, there exists a very narrow composition (heptane content) for which the flocculation process is sufficiently slow to be observed conveniently. In addition, it is worth mentioning that variations in aggregate sizes and masses are observed to be much larger when varying solvent composition (by heptane addition¹⁵) than those observed after cooling. These previous experiments, together with the ones reported in this paper, suggest that the process of asphaltene structural evolution and flocculation is similar under temperature or composition variations, even though their amplitude and kinetics may be different.

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